SYNTHESIS, CHARACTERIZATION AND APPLICATIONS OF LANTHANIDE DOPED ZINC OXIDE NANOPARTICLES

A

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IN

CHEMISTRY

UNDER THE FACULTY OF SCIENCE

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PROPOSAL FOR TOPIC APPROVAL TO BE SUBMITTED TO THE UNIVERSITY OF MUMBAI FOR THE PH. D DEGREE IN THE SUBJECT OF CHEMISTRY.

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INDEX

Sr. No.	Contents	Page No.
1	Title	3
2	Aims of the Study	3
3	Objectives of Study	3
4	Study Background and significance of study	4
5	National Status	6
6	International Status	7
7	Study Hypothesis	8
8	Study Rationale	9
9	Research Methodology	10
10	Statistical Plan	12
11	Limitations of the Study	12
12	Expected Outcomes of Study	13
13	Bibliography	14 -17

1. **Title:** Synthesis, Characterization and Applications of Lanthanide doped zinc oxide nanoparticles.

2. **Aims of the study:** To Synthesize and Characterize lanthanide doped zinc oxide nanoparticles and its Applications in various fields of science.

3. **Objectives of the study:**

- To study lanthanide doped zinc oxide nanoparticles for a variety of activities like photocatalytic, sensor, antimicrobial etc.
- To synthesize sample using sol-gel technique, microwave technique, solvothermal technique, micro emulsion technique, chemical reduction technique, hydrothermal technique, sonochemical technique, ultrasonic technique etc.
- To characterize sample using UV- visible Diffuse Reflectance Spectroscopy (UV-vis-DRS), X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM).
- To analyse surface morphology and to investigate the size and shape of the synthesized compounds/ nanoparticles using Scanning Electron Microscope and Transmission Electron Microscope.
- To support the claim made by XRD, SEM, TEM and other instruments such as UV-Visible spectrophotometer, Infra-Red Spectrophotometer and particle size analyser will also be used.

- To test controlled size and shape of Zinc based nanocomposites for the decomposition of organic and inorganic pollutant under UV, Visible and Solar light.
- The optimized nanocomposites will be used as a photocatalyst for the hydrogen generation.

4. Study Background and significance of the study:

Metal oxide nanoparticles have widespread technological and industrial importance because of their unique structure and optical, electrical, magnetic and mechanical properties. These properties enhance the stability and thermal strength of metal oxides. Metal oxides play a significant role in a variety of applications such as biomedical, photocatalytic, microelectronic devices, sensors, solar cells, coatings, catalysts, optoelectronic devices, antimicrobial activities, etc. They exhibit metallic, semiconducting or insulating behaviour based on the band gap. A number of metal elements are capable to form the different number of oxide compounds, which can take up number of structural geometries with an electronic structure that can demonstrate various exciting properties.

The basic philosophy behind the advancement of science lies in selecting, customizing and applying appropriate elements within the periodic table, which is the absolute gift from nature to the bio life. Transition elements enable its application in a wide arena like catalysis, bio mimics, energy sector, food industry, etc., owing to the presence of variable oxidation states. Surprisingly, *Zn* is an essential trace element for bio life among the Zinc family, which is the primary active metal involved with numerous enzymes like carbonic anhydrase,

carboxypeptidase and alcohol dehydrogenase. However, Cadmium and Mercury with similar electronic configurations belonging to the same family are toxic in larger proportions for bio life.[1]

Among numerous metal oxides, *ZnO* is a widely used semiconductor compound. It bears the important traits of low cost, higher chemical stability, mass production and topical drug component.[2]

ZnO is also widely applied as a photocatalyst that undertakes a large cluster of potential; chemical, photochemical and electrochemical responses.[3] The primary parameters subjected to tailoring for variable application are surface area and surface defects, which govern semiconductor *ZnO*'s photocatalytic activity.

In addition, doped *ZnO* nanoparticles functions well as the favourable catalyst for the degradation of organic pollutants due to their high surface activity, morphological features and feasibility to tailor/induce the defect-driven phenomena.[4]

Doped *ZnO* nanoparticles have been reported to exhibit excellent sensing properties for both oxidizing and reducing gases due to its distinctive property of differentiating between oxidizing and reducing gas molecules that lies in the surface reaction.

Some metal oxides NPs are stable under harsh processing conditions and have selective toxicity to bacteria but also exhibit a minimal effect on human and animal cells.[5–7] For example, *ZnO* NPs which are nontoxic and biocompatible, have been utilized as drug carriers, cosmetics ingredients and medical filling materials.[8,9]

Recently, *ZnO* NPs were found to have antibacterial activity against important food borne pathogens. [5,10]

5. National Status:

Aneesh et al., (2007) have prepared zinc oxide nanoparticles using the hydrothermal method by varying different physical conditions. The zinc oxide nanoparticles have been examined by XRD, TEM, SAED, ICP-AES, DRS and PL measurements. The PL measurements have been confirmed the presence of interstitial defects.[11]

Kumbhakar et al., (2008) have synthesized zinc oxide nanoparticles using zinc nitrate as a precursor by chemical method. The prepared nanoparticles have been confirmed by XRD, TEM, SEM, EDAX, UV-Vis and PL measurements. The average particle size has been estimated as 2.1 nm using effective mass model.[12]

Krishnakumar et al., (2009) have reported synthesis of zinc oxide nanostructures by microwave assisted method for carbon monoxide sensing applications. The zinc acetate has been used as a source material. The nanostructures have been examined using SEM, TEM and XRD analysis. The high sensitive carbon mono oxide gas sensor has been fabricated.[13]

Karunakaran et al., *Ce*-doped *ZnO* nanoparticles were tested first as a photocatalyst forcyanide photo-oxidation and then as an antimicrobial agent against E. coli.[14] The authors reported an increased bactericidal activity in dark conditions for the doped *ZnO* NPs which was related to the physical attachment of the particles on the bacteria membranes. Other examples are terbium and

gadolinium.[15] Both were tested in terms of photocatalytic activity, evaluating the efficiency in Victoria blue degradation and in terms of the antibacterial activity against S. Aureus.[15] In both the cases, increased performances were found with respect to pure *ZnO*.

6. International Status:

Peng et al., (2006) have reported the synthesis of *ZnO* nanoparticles using the sol-gel method. The zinc acetate has been used as source material. Zinc oxide nanoparticles have been characterized by XRD, TEM, UV and PL measurements. The presence of oxygen defects has been detected in the prepared nanoparticles.[16]

Liu et al., (2011) have fabricated pinecone-shaped zinc oxide nanostructures on *Si* substrates by pulsed laser deposition. An Nd-YAG laser with 335 nm has been used in the preparation process. The nanostructures have been investigated by XRD, SEM, Raman and XPS studies. The pinecone-shaped zinc oxide nanostructures have been found suitable for oxygen gas sensors.[17]

Jiang et al., have reported that *Eu (III)* behaves as a shallow electron trap with the *Eu (II)* fundamental energy level slightly below the *ZnO* conduction band, which can cause the generation of a *ZnO* → *Eu (III)* energy transfer. However, the primary limitation lies in the insertion of lanthanide ions into *ZnO*, owing to the difference in ionic radii, charge, and coordination number.[18, 19]

7. Study Hypothesis:

Zinc oxide nanoparticles (*ZnO* NPs) are deeply investigated due to their peculiar physical and chemical properties. Also, for the large surface to volume ratio, coupled with a reduced size, antimicrobial activity, photocatalytic and semiconducting properties.

The main advantages in synthesis of lanthanide doped *ZnO* nanoparticles are the use of non-toxic solvents, low synthesis temperatures, and the use of simple equipment in the Microwave assisted hydrothermal, wet chemical- sol gel/ hydrothermal method. Moreover, due to the relatively good purity and resulting stoichiometry of the product, wet chemical methods appear to be a promising choice for the development of doped *ZnO* nanoparticles. The inclusion of the dopant can be obtained in a practically straightforward way by mixing the dopant ion solution together with the zinc precursor solution, before mixing with the base. The morphology and the dimension of the nanoparticles can be controlled through surfactants. The use of different surfactants in different amount will help in demonstrating change to the morphology of the particles resulting in the distortion of the crystals. This distortion of the crystalline cell will help in enhancing the piezoelectric coefficient.

The reverse-micelles microemulsion method can also be explored for the preparation of doped *ZnO* nanoparticles. The presence of specific surfactants by this approach can lead to peculiar *ZnO* morphologies, such as hollow structures, and can also limit the dimensions of the particles during nucleation.

To summarise above studies doping represents a valuable tool in extending the use of *ZnO* NPs as promising photocatalyst and antimicrobial agent for practical applications.

8. Study Rationale:

Over the decades, *ZnO* has been considered as one of the promising photocatalyst due to its high chemical stability, high photostability, non-toxicity, low cost and high efficiency in photocatalysis.[20] Current findings suggest that efficiency of *ZnO* can be increased by doping it with rare earth materials.[21] This technique has been approached and it is proven that the photocatalytic efficiency of ZnO increases through doping with some elements including *Cerium - Ce*[22],*Europium - Eu*[23] and *Dysprosium - Dy*.[24] However, the effect of using lanthanides as dopant in *ZnO* based photocatalyst is somehow limited compared to transition metal dopants. Hence, this study presents the investigation of the photocatalytic properties of lanthanide-doped *ZnO*.

As per the studies, nearly 5% of the incoming solar energy in all part of the solar spectrum, while the rest is visible light[25]. It is therefore of great significance to develop a material that can absorb both UV and Visible light to widen the range of a photocatalyst. In almost on photocatalytic materials, the band gap of the semiconductor metal oxide plays a vital role in triggering the photo reaction after UV- induced electron hole pair.[26] Many studies have been sited showing that doping of metals can cause a hyperchromic shift in the optical absorption of semiconductor metal oxides. Usually doping is done to create tail states within the band gap.[27]

Overall, the dopant is favourable in importing and tailoring the electrical changes, narrowing of band gap, significant impact on crystallinity with possible increased optical absorption range.

Pure *ZnO* nanoparticles have been extensively used as antibacterial agents due to their Photo-oxidizing and photocatalytic properties. Its antimicrobial properties can be tailored in several ways: parameters like morphology, size, concentration, surface defects and fictionalization all contribute to change the performances of *ZnO* nanoparticles in this field.[28]

9. Research Methodology:

Synthesizing Methods

Lanthanide doped zinc oxide nanoparticles can be synthesized by using following methods/techniques depending on the different physical and chemical properties.

- Sol-gel technique
- Microwave technique
- Solvothermal technique
- Microemulsion technique
- Chemical reduction technique
- Hydrothermal technique
- Sonochemical technique
- Ultrasonic technique
- Laser-aided technique
- Green synthesis

The compounds will be characterized using the following methods/ instrumentation:

- Infrared vibrational spectroscopy
- X-Ray diffraction analysis (XRD)
- Ultraviolet-visible spectroscopy
- Scanning Electron Microscopy (SEM)
- Transmission Electron Microscope (TEM)

Other necessities include:

- Teflon Lined Hydrothermal Autoclave
- Hot Air Oven
- Magnetic Stirrer

Some basic solvents like ethyl alcohol, Distilled Water and other common glass wares from the laboratory.

10. Statistical Plan:

1st Year	2nd Year	3rd Year
➢ Literature survey ➢ Finalization of Scheme ➢ Procurement of costly raw material ➢ Attending courses for Research credits ➢ Attending National and International Research Conference ➢ Optimization of Zinc Oxide Nanoparticles for its composites. ➢ Writing Review Paper ➢ Experimental Setup	➢ Synthesis of lanthanide doped zinc oxide ➢ Attending National and International Research Conference ➢ Research Presentation ➢ Attending courses for Research credits ➢ Paper Publication	➢ Synthesis and Characterization of prepared zinc doped nanocomposites ➢ Optimization of zinc doped nanocomposites towards photocatalytic activity ➢ Paper Publication ➢ Results and Conclusion based on Analysis ➢ Writing and Thesis

11. Limitations of the study:

Over the years, a wide variety of chemical, physical and hybrid methods for the synthesis of safer and more sustainable production of *ZnO* NPs has been reported. However, these approaches still present some limitations, such as the usage of highly toxic and hazardous chemicals are used for the synthesis of doped and undoped *ZnO* NPs.

12. Expected outcome of the study:

Doping ZnO NPs with lanthanide opens a wide diversity of alternatives to undoped *ZnO* NPs due to their advantages in terms of safety, sustainability and environmental compatibility. This work focuses on developing a safe and sustainable route for the scalable production of nanomaterials, maintaining photocatalytic properties. We believe that the study of synthesis is still at its early stage. Many of the concepts and ideas are not explored to the fullest. Utilization of cost-effective methods has hardly been used. Moreover, the effectiveness of lanthanide doped zinc oxide nanomaterials have not yet been fully demonstrated to be the alternative for the synthetic methods found in both bulk and fine chemical industries. From this research, we are hoping to provide an insight of lanthanide doped zinc oxide nanomaterials with excellent photocatalytic activity and antimicrobial activity.

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